Synthesis and Characterisation of Hydroxyl-terminated Liquid Natural Rubber by Photo-Fenton Reaction

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Hydroxyl-terminated liquid natural rubber (HTNR) was prepared by the photo-Fenton reaction, which was carried out in solution in the presence of $\text{H}_2\text{O}_2/\text{Fe(II)}$ combined with UV irradiation. The HTNR obtained was characterized by GPC, FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, DEPT-NMR spectroscopy as well as by chemical methods. A probable mechanism leading to the formation of HTNR was discussed based on the analytical data.

Key words: Synthesis; natural rubber; liquid natural rubber; FT-IR; gel permeation chromatography (GPC); epoxy; UV irradiation

Basically, the methods for the preparation of liquid natural rubbers (LNRs) involve controlled degradation or depolymerization of the natural rubber (NR) backbone via oxidative chain scissions by either chemical or photochemical routes. Thus far, several methods leading to the production of LNRs have been developed and can be placed into three main categories, i.e. redox, photochemical degradation and oxidation at high temperature and pressure. Of these methods, the redox and photochemical methods have received the most attention (Ravindran *et al.* 1988).

According to the first method, NR in the latex stage or in an organic solvent was degraded on a large scale by the redox reagent phenylhydrazine and atmospheric oxygen at $50^\circ\text{--}70^\circ\text{C}$. The method yielded LNRs with terminal carbonyl groups which in the presence of excess phenylhydrazine were transformed into phenylhydrazones (Nor & Ebdon 1988). Concerning the photochemical method, Gupta *et al.* obtained hydroxyl-terminated

liquid natural rubbers (HTNRs) using hydrogen peroxide as the reagent at high temperature and pressure, while Ravindran and co-workers reported the production of HTNRs by photochemical depolymerization of NR toluene solution at room temperature in the presence of H_2O_2 and homogenizing agents such as methanol and THF (Ravindran *et al.* 1988; Nor & Ebdon 1988).

It is well known that the catalyzation of hydrogen peroxide by ferrous sulfate, Fenton's reagent, is one of the most common advanced oxidation processes. Fenton's reaction is defined as the catalytic generation of hydroxyl radical resulting from the chain reaction between ferrous ion and hydrogen peroxide, and organic compounds could be oxidized according the chain reaction mechanism (Kang & Kwang 2000; Zhang *et al.* 2005). Recent reports indicate that a combination of $\text{H}_2\text{O}_2/\text{UV}$ irradiation with Fe (II), the so-called the photo-Fenton process, can significantly enhance decomposition of a variety of organic compounds, including

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depolymerization of a variety of polymers, such as the different copolymers of acrylamide and acrylic acid (Mai *et al.* 2002), polychloroprene (Freitas *et al.* 2005), aminosilicone polymer (Teixeira *et al.* 2005), NR and polychloroprene/NR blends (Freitas *et al.* 2008), and PVA (Lei *et al.* 1998; Giroto *et al.* 2006).

In this paper, we report some results that concern the preparation of HTNR by the photo-Fenton reaction, the characterization of the HTNR obtained by GPC, FTIR, ^1H -NMR, ^{13}C -NMR spectroscopy as well as by chemical methods. The mechanism of depolymerization and hydroxylation of NR to form HTNR based on the analytical data is also discussed in this study.

EXPERIMENTAL

Materials

Natural crumb rubber (SVR20, $M_n \sim 780,000$) was supplied by the Dong Duong Group, Vietnam. Toluene, methanol, and tetrahydrofuran (THF) were of reagent grade and used as received. Hydroquinone ReagentPlus® from Aldrich was used. Santowhite MK, the non-staining antioxidant and phenyl- β -naphthylamine were obtained from Merck. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 (30%, w/w), H_2SO_4 , were also purchased from Merck. All other chemicals and solvents were of purest grade commercially available and used without further purification.

Experimental Procedure

Natural crumb rubber was masticated for 30 min at 40°C . 10 g of it was dissolved in 100 ml of toluene and the solution was charged in a reactor, a flat-bottomed borosilicate glass flask of 250 ml capacity fitted with a water condenser, a magnetic stirrer and a water bath. Precise amounts of Fenton reagent (Fe (II) and H_2O_2) were added dropwise and continuously stirred with a magnetic bar. The mixture was homogenized to a certain extent by the addition of 25 ml of THF.

The pH of the solution was adjusted with H_2SO_4 and /or NaOH solution in THF. All experiments were conducted at $\text{pH} \sim 2.5\text{--}3.0$, and the $\text{H}_2\text{O}_2/\text{Fe (II)}$ molar ratio was maintained at 1.5 because these values were optimum for the photo-Fenton reaction (Piglatello *et al.* 1999; Giang 2010). The reaction temperature was varied from 30°C to 70°C using a water bath for a reaction time period of 1 h to 50 h.

For the experiment, a 160 W high pressure Hg lamp was used as a UV light source. The beam was parallel and the length between the lamp and the reactor wall was 3 cm.

After about 32 h of irradiation, 0.2 g hydroquinone (about 0.02% w/v of the reaction mixture) was dispersed in the solution and that was allowed to stand for a certain time. A layer of water separated at the bottom along with some white deposits as by-products. These were removed, and liquefied rubber was recovered from the top toluene layer by distilling off the solvent under low pressure. The product was finally washed successively with water and methanol, treated with 0.6% w/w Santowhite MK antioxidant and finally vacuum dried. The sample for analysis was purified further by repeated precipitation of methanol from the toluene solution and dried in a vacuum oven. The by-product was finally washed with methanol and dried in a vacuum to obtain a 7%–8% yield of highly viscid material.

Measurements

The molecular weights and molecular weight distribution of the original NR as well as those of the HTNRs were determined by a gel permeation chromatography (GPC) system equipped with a series of PL aquagel-OH columns (one Guard $8\ \mu\text{m}$, $50 \times 7.5\ \text{mm}$ and two MIXED $8\ \mu\text{m}$, $300 \times 7.5\ \text{mm}$, PLL Laboratories, UK), and a refractive index (RI) detector (RI2000-F, SFD, Torrance, CA), using polystyrene standards of different molecular weight and narrow polydispersity to produce a

calibration curve. The mobile phase was 1.0 ml/min, and the columns and the RI detector cell were maintained at 30°C. The molecular weight (M_n) of the original NR, as determined by the above-mentioned methods, was about 780 000. A sample of HTNR having $M_n \sim 3060$ was used throughout this study for characterization by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, DEPT-NMR and FTIR analyses. This sample of HTNR would also be used to modify bisphenol-A diglycidyl ether-based epoxy (DGEBA), the results of which were going to be published in the other article in this issue of *ASEAN J. Sc. Technol. Dev.*, pp. 22–28.

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and DEPT-NMR spectra of the investigated samples were recorded from a solution in CDCl_3 using NMR spectrometer (NMR-Brucker-500 MHz). FTIR analysis was performed on a FTIR IMPACT 410 spectrometer and the samples were scanned from 400 – 4000 cm^{-1} .

Hydroxyl, hydroperoxide, carboxyl, and carbonyl groups were estimated using standard methods (Krause *et al.* 1983).

RESULTS AND DISCUSSION

Characterization of Hydroxyl-terminated Liquid Natural Rubber (HTNR)

The original natural rubber (NR) and the product obtained by the photo-Fenton process, HTNR, were analyzed by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, DEPT-NMR, and other chemical methods.

The following absorptions were observed in the IR spectra, both of the original NR (*Figure 1a*) and of HTNR (*Figure 1b*): 3032 cm^{-1} (m), 2958 cm^{-1} (s), 2862 cm^{-1} (s), 2726 cm^{-1} (s) (C-H str.); 1661 cm^{-1} (m, C=C, *cis*-vinylene); 1446 cm^{-1} (s), 1377 cm^{-1} (s) (C-H def.); 891 cm^{-1} (m, $-\text{CH}_3$ def.); 842 cm^{-1} (s, C-H out of plane def. in $-\text{CHR}=\text{CCR}^1$).

Apart from the major IR absorption band characteristics for *cis*-1,4-polyisoprene (*cis*-1,4-PIP), other IR absorptions were also observed in the FTIR spectrum of HTNR (*Figure 1b*): a broad absorption band at 3600–3400 cm^{-1} , characteristic of OH stretching vibration; an absorption band at 1310 cm^{-1}

Figure 1. FTIR spectrum of (a) NR and (b) HTNR prepared by the photo-Fenton process.

(m, C-O str., aliph. primary alcohol) that confirmed the presence of primary hydroxyl groups in the depolymerized product, i.e. in the HTNR.

The ^1H -NMR and ^{13}C -NMR spectra in CDCl_3 at 28°C of the depolymerized product (Figures 2a, b and 3a, b) lent further support to the above conclusion. ^1H -NMR: $\delta = 1.679$ p.p.m. [s; $-\text{CH}_3$ (5), 3H]; $\delta = 2.042$ p.p.m. [brs; $-\text{CH}_2$ -(1) and $-\text{CH}_2$ -(4), 4H]; $\delta = 5.125$ p.p.m. [m; CH (3), 1H]. The spectrum also contained minor peaks at δ from 1.254 ppm to 1.611 p.p.m., indicating the probable presence of side products. A minor peak was observed at around $\delta \sim 2.69$ ppm (Figure 2b) in the ^1H -NMR of HTNR prepared by the photo-Fenton reaction due to the formation of an epoxy group, i.e. the proton attached to the oxirane ring (Burfield *et al.* 1984), whereas it was not observed in the ^1H -NMR of the original NR (Figure 2a).

The signal due to the hydroxyl proton in the hydroxymethyl group is usually observed around $\delta = 4.0$ p.p.m. to 4.2 p.p.m. This however, could not be detected in the present case, since the signal / noise ratio was too unfavorable to see the end groups.

The ^{13}C -NMR spectrum indicated ^{13}C shieldings, typical of *cis*-1,4-PIP at the following positions: C^1 : $\delta = 32.23$ p.p.m.; C^2 : $\delta = 135.16$

p.p.m.; C^3 : $\delta = 125.03$ p.p.m.; C^4 : $\delta = 26.38$ p.p.m.; C^5 : $\delta = 23.4$ p.p.m. (Equation 10).

Apart from these major peaks the spectrum also contained minor peaks at $\delta = 78.39$, 76.98 and 75.57 p.p.m. due to CDCl_3 . Other minor peaks at $\delta = 60.847$ and 64.540 p.p.m. could be due to α -carbons attached to the hydroxyl groups in structures like (I) and (II), respectively and hence could indeed correspond to an α -hydroxymethyl group. The allylic hydroxyl protons in the ^1H -NMR spectra were masked by the multiples at $\delta = 5.125$ p.p.m. of the $>\text{C}=\text{C}-\text{H}$ protons (Equation 9). Several minor peaks could also be observed at δ from 2.00 to 3.53 p.p.m. in the ^{13}C -NMR spectrum of HTNR (Figure 3b), indicating the probable side products due to the formation of epoxy group.

The broad OH stretching band at 3600 cm^{-1} – 3400 cm^{-1} in the FTIR spectrum of the HTNR (Figure 1b) and also the peaks at $\delta = 60.847$ p.p.m. and 64.540 p.p.m. (Figure 3b) which were characteristic of the α -carbons of allyl alcohol in the ^{13}C -NMR spectrum of HTNR suggest the terminal hydroxyl groups in the product. The allylic hydroxyl protons in the ^1H -NMR spectra were masked by the multiples at $\delta = 5.125$ p.p.m. of the $>\text{C}=\text{C}-\text{H}$ protons.

All the other signal characteristics for both NR and HTNR were observed in the ^1H -NMR

Figure 2. ^1H -NMR spectrum of NR(a) and HTNR(b) prepared by the photo-Fenton reaction.

Figure 3. ^{13}C -NMR spectrum of NR (a), and HTNR (b), prepared by the photo-Fenton process.

spectrum (Figures 2a, b): $\delta = 5.08$ p.p.m., ($=\text{CH}$); $\delta = 2.00$ p.p.m., ($-\text{CH}_2-$); $\delta = 1.67$ p.p.m., ($-\text{CH}_3$), as well as in the ^{13}C -NMR spectrum (Figure 3): $\delta = 135.012$ p.p.m., (C_2 atom); $\delta = 124.900$ p.p.m., (C_3 atom); $\delta = 32.216$ p.p.m., (C_1 atom); $\delta = 26.409$ p.p.m., (C_4 atom); and $\delta = 23.433$ p.p.m., (C_5 atom). The *cis*-1,4-PIP configuration of both NR and LNRs were preserved in the DEPT-NMR spectrum (Figure 4). The main absorption bands, characteristic of NR, were also preserved in the FTIR spectra. All these indicated that the *cis*-1,4-PIP configuration was not disturbed during the depolymerization process. Further evidence was the fact that there was no observed change in the absorption band of the isoprene unit, i.e. at 836 cm^{-1} in the FTIR spectrum (Figures 1a, b).

The hydroxyl value estimated for HTNR was 27.12 mg of KOH / g, which gave it a hydroxyl functionality of 1.97–1.98. The product readily reacts with diisocyanates such as toluene diisocyanate, leading to chain extension.

Mechanism of Depolymerization of NR by the Photo-Fenton Process

It is well known that in the photo-Fenton process, the reaction between H_2O_2 and ferrous salt, i.e. the Fenton reaction, the primary reactions in representative Fenton process are (Yang *et al.* 2005).

As seen from Equations 1 and 2, the decomposition of H_2O_2 by iron ions is through the interaction between Fe^{2+} and Fe^{3+} . As the reaction rate in Equation 1 was faster than that of Equation 2, Fe^{2+} was rapidly oxidized to Fe^{3+} in the reaction process. Therefore, the concentration of $\cdot\text{OH}$ in the solution rapidly increased and could degrade the NR macromolecule. In addition, from Equation 2 it could be seen that Fe^{2+} could be re-generated from the reduction of Fe^{3+} , leading to the continuous generation of $\cdot\text{OH}$. The combination of thermal process and UV irradiation enabled the oxidation power of Fenton reagent to be significantly increased due mainly to the photo-reduction of Fe(III) to Fe(II) , which could react with H_2O_2 establishing a cycle mechanism of generating additional $\cdot\text{OH}$ by Equation 3.

Figure 4. DEPT spectra of HTNR prepared by the photo-Fenton reaction.

The hydrogen peroxide used in the degradation process is susceptible to decomposition under the influence of radiation. Although hydrogen peroxide has an absorption maximum at 254 nm; it interacts with radiation up to 370 nm, yielding hydroxyl radicals. If hydrogen peroxide and hydroxyl radicals were in excess, competitive reactions could take place (Yang *et al.* 2005). Hydroxyl radicals are prone to recombination or to reactions according to the following schemes:

Ravindran and co-workers (1988) have demonstrated the existence of *Structures 1* and *2* in the depolymerized products:

Structure 1

Structure 2

The generation of such structural entities entails the cleavage of the original rubber molecule between the α -carbon atoms. In the case of NR, the σ bond between α -methylene groups which connect the isoprene units are not in the same plane with the double bonds. This is because there is a tendency of coiling up of the rubber segments due to its *cis* configuration (Structure 3):

Structure 3

The steric hindrance caused by such an unbalanced structure with pendent methyl groups weakens the $-\text{CH}_2-\text{CH}_2-$ bond, leading to its rupture under certain conditions which could be provided by thermal energy or chain modifications caused by radical species or by radiation.

Based on the above analytical data, the mechanism for the depolymerization of NR

by the photo-Fenton process leading to the formation of HTNR could be suggested to be as below (Structure 4).

CONCLUSIONS

Hydroxyl-terminated liquid natural rubber (HTNR) was successfully prepared by the Photo-Fenton reaction, which was carried out in solution in the presence of $\text{H}_2\text{O}_2/\text{Fe(II)}$ combined with UV irradiation. The HTNRs obtained were characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and DEPT-NMR spectroscopy as well as by chemical methods. A probable mechanism leading to the formation of HTNR was discussed based on the analytical data.

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